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EFFECT OF ELECTROLYTE COMPOSITION ON POROUS ANODIC ALUMINIUM OXIDE FORMATION

The effect of composite anodizing electrolyte with reduced content of organic acids on the formation rate, structure and properties of aluminium oxide film was studied. It is established that for the production of electronic devices structural parts of improved insulation properties it is preferable to use the solutions where less active citric acid predominates. It has been shown that kinetic retardation of specified anodic process of aluminium oxidation increases the density of barrier oxide while preserving the rate of main porous Al_2O_3 layer growth.

Introduction. Modern tendencies in the development of electronic devices are often related with implementation of integral approach to designing and fabrication of new products. This is especially true of microelectromechanical systems (MEMS) combining microelectronic, micromechanical, sensor and other components. These devices are distinguished by multifunctional performance, tiny size, producibility, low power consumption and cost. Manufacture of such products puts forward new requirements to the characteristics of dielectrical structural parts (substrate, membrane, spacer). These are usually formed being based on such materials as SiO_2, Si_3N_4, Al_2O_3.

Lately both in microelectronics and nanoelectronics electrochemical processes that permit the formation of continuous and segment films and other structures of various chemical nature (metals, simple and complex oxides, composites) and size have been extensively used and improved. Electrochemical technology of anodic aluminium oxide (AAO) preparation is suitable for the production of micro- and nanosize devices with planar and voluminous elements of various spatial configuration [1]. It is important that the technology concerned is compatible with integral planar microelectronics technology. Anodic aluminium oxide (AAO) is a self-arranging structure with spatial parameters inaccessible for modern technologies such as, for example, photolithography ones. AAO-based films, substrates and wafers have spatial-porous structure. Presence of large quantity of micro- and nanosize pores being sufficiently uniform and controlled within a wide range of dimensions perpendicular to the boundary surfaces makes it possible to use AAO as a functional and as a model material. Possibility of specified control of phase transformation processes in anodic aluminium oxide ensures performance characteristics variation in the AAO-based materials. Essential difference of AAO from anodic oxides of other materials is the wide range of film thicknesses (from 10 to 500 μm).

The aim of the investigation was the study of the effect produced by the composition of composite Al anodizing electrolyte with reduced content of organic acids on peculiarities of the formation of AAO for electronic devices.

Main part. Preparation of porous AAO samples was performed by multiple stage technology. As source material A99 aluminium in the form of 0.08–0.1 mm thick band was used. Preparation of aluminium blanks involved consecutive degreasing in boiling benzine and acetone, drying, planarizing lining between the slabs heated to the temperature of around 200°C, electropolishing in H_3PO_4 : CH_3COOH = = 1 : 1 and baking at the temperature of 220°C. The next phase of samples preparation was preliminary galvanostatic anodizing in 3% solution of oxalic acid at electrolyte temperature of 45°C and current density of 15 mA/cm^2 during 50 s. Then the primary oxide film was stripped in chrome-phosphoric solution.

The final stage of AAO preparation was performed in the composite electrolytes containing more reactive oxalic acid, $C_2H_2O_4$, and less active citric acid, $C_6H_8O_7$, in various proportions (Table 1). By the character of its interaction with aluminium oxide this electrolyte falls into the second group of the solutions where Al_2O_3 is poorly dissolved. Such electrolyte allows producing the oxide films of 1–300 μm in thickness with their high insulation properties [2]. For AAO application as an insulator it is necessary to obtain the oxide with minimum possible remnants amount (water, acids). Therefore, for the anodizing process the composite electrolyte with the lowest temperature, acid concentration and increased currents density characteristics was chosen.

The anodizing process was performed in experimental test bath with water cooling jacket and electrolyte mixer under galvanostatic conditions, with current density and temperature being 7 mA/cm^2 and 11–12°C, respectively, for 200–230 min. The average rate of oxide film growth accounted for 0.23 μm/min. During the anodizing process chronovoltaic dependences were registered (Fig. 1).

Table 1

Acid content in composite anodizing electrolyte

Electrolyte number	$C_2H_2O_4$, wt %	$C_6H_8O_7$, wt %
1	3	–
2	3	1
3	2	2
4	1	3
5	0.5	1.5
6	0.5	1
7	0.35	1
8	0.2	0.8

Separation of AAO film from metal substrate was performed by multiphase chemical etching of the back side of samples first in concentrated NaOH solution, then in HCl + $CuCl_2$ solution and finally in HNO_3 for removing copper. The last stage of porous AAO samples preparation was heat treatment at the temperature of 900°C for crystallizing the originally amorphous product. The thicknesses of AAO samples obtained were measured by means of a digital caliper with inductive converter.

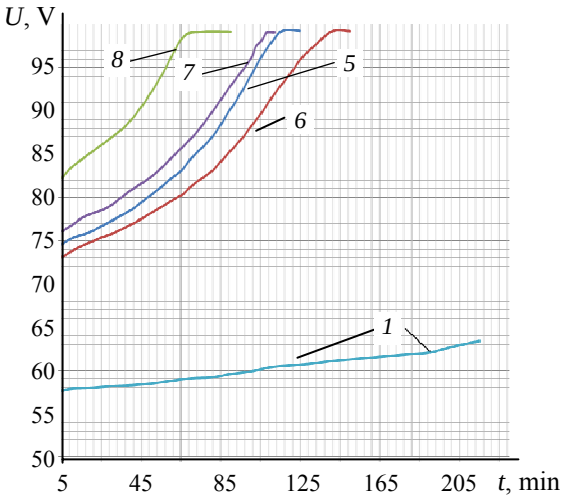

Fig. 1. Chronovoltaic dependences of anodizing process in various electrolytes. Number of the line indicates the electrolyte number in Table 1

The character of the obtained chronovoltaic dependences of aluminium anodizing processes in various electrolytes (Fig. 1) corresponds to the data for anodizing processes in galvanostatic mode [3]. In this case the initial anodizing voltage is set in electrolyser for 1–5 min, then the slope of chonovoltaic dependence decreases (the first section on the curves of Fig. 1) and finally constant anodizing voltage is set, it being approximately to 100 V in our experiments.

Such kind of $U = f(t)$ dependences is determined by a well-known structure of anodic oxide consisting of internal non-porous and external porous layer of oxide. At the preparation of porous AAO-based materials with controlled sizes of micropores it is relevant to consider the oxide growth including four phases:

1) irregular (uneven) formation of barrier non-conductive oxide film (($\Omega = 10^{10}$–10^{12} Ohm · cm) on metal surface;

2) redistribution of electric fields intensity over sample surface coated with non-conductive oxide;

3) selective solution of the forming oxide in the centers close to the metal surface due to increased electric field intensity and/or local heating;

4) regular (even) growth of porous AAO due to self-balancing concurrence between centers of oxide solution on the surface.

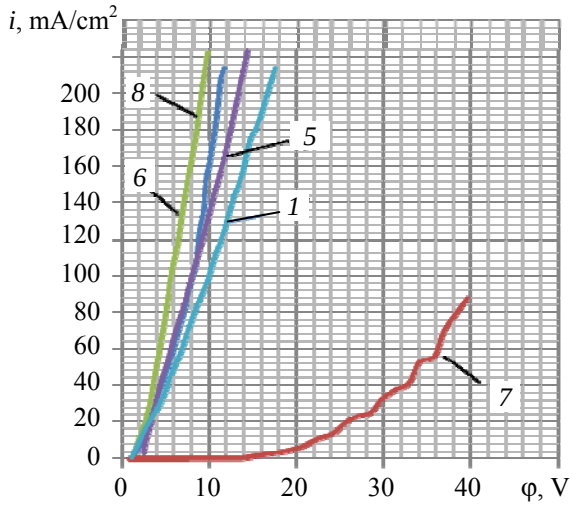

Fig. 2. Anodic polarization curves of aluminium electrode in the electrolytes of various composition. The curve number indicates the electrolyte number according to Table 1

Thus, increase in the initial anodizing voltage which value is actually determined by voltage fall in non-conductive barrier oxide has positive effect on insulating properties of porous AAO. In our experiments the increased values of initial anodizing voltage are fixed in the electrolytes, firstly, with decreased total acid content and, secondly, with citric acid predominating (electrolytes N 5–8 from Table 1). These electrolytes are preferable for producing dielectric insulating elements. However, when used as substrates sufficient thickness of the material is essential. Considering these requirements, it is in electrolyte N 5 that oxide thickness of above 40 μm is obtained at sufficiently high initial anodizing voltage of around 75 V.

The peculiarities of porous AAO formation in composite electrolytes were investigated with the

help of polarization curves. The investigations were carried out in a three-electrode electrochemical cell with three voltmeters and power supply in controlled potential conditions within 2–48 V voltage range. Source aluminium was used as the main electrode, saturated chloroargentum being used as a reference electrode and Pt – as an auxiliary one. The measurements were done in the electrolytes suitable for preparing films having enhanced resistance and thickness, i.e. in the electrolytes N 5–6 (Table 1). In almost all the cases the anodic polarization curves obtained are of ohmic nature that is determined mainly by the voltage fall in the oxide film as compared with the electrode polarization. Oxidation process in electrolyte N 7 is marked with maximum kinetic retardation of electrochemical nature, that correlates with the data of Table 2.

Table 2

Parameters of oxide films growth in various electrolytes

Electrolyte N	Oxide thickness, μm	Initial anodizing voltage, V
1	45.8	57.6
2	43.3	55.7
3	46.0	57.3
4	44.8	63.8
5	40.1	74.4
6	42.6	73.1
7	33.8	76.2
8	28.8	82.4

Probably, in the electrolyte mentioned barrier oxide of low conductance is formed resulting from the enhanced initial anodizing voltage. However kinetic retardation of the electrode processes reduces the rate of barrier oxide growth on the metal surface.

Conclusion. Investigation of the processes of anodic aluminium oxide preparation from composite electrolytes with reduced content of organic acids revealed that for producing electronic devices structural parts, for example MEMS, gas sensors, possessing improved insulation properties it is preferable to use the solutions in which less active citric acid predominates.

Kinetic retardation of specified anodic process of aluminium oxidation results in higher density of barrier oxide while preserving the growth rate of main porous Al_2O_3 layer.

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